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Modelling sulfide fluxes and Cu canister corrosion rates in the engineered barrier system of a spent fuel repository

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Abstract

Sulfide is a corrodant for the copper canister in the planned spent fuel repository in Finland and Sweden. Sulfide fluxes and canister corrosion rates in the clay barrier have been assessed by a reactive transport model using the geochemical simulator PFLOTRAN. These rates are linked to the dissolution of gypsum, present in the clay backfill, and the fluxes of sulfate, organic carbon and Fe(II) into interface zones where microbial activity occurs. The permeability of the rock adjacent to the clay backfill exerts a strong control on the biogeochemical processes and the resulting copper corrosion rates.

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1. Introduction

Microbial sulfate reduction is a common process in anaerobic environments. This process is of concern in the spent fuel repository (referred to as KBS-3) in Finland and Sweden because sulfide is a corrodant of the Cu canister holding the waste¹. In the KBS-3 concept, the Cu canisters are surrounded by smectite-rich compacted bentonite (referred to as buffer) in vertical deposition holes hosted by crystalline rock (Fig. 1). The deposition tunnels above are backfilled with lower grade (smectite-poorer) clay material (referred to as backfill). This material contains soluble minerals, such as gypsum which is a potential source of sulfide via bacterial sulfate reduction. In this study, (i) the fate of gypsum in the backfill, (ii) the diffusion and reduction of sulfate and the pathways of sulfide, and finally (iii) the corrosion rates of the Cu canister have been assessed by reactive transport modelling.

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2. Model setup

The overall processes are conceptualized in a step-wise manner by considering first the backfill-rock system without deposition holes separated by an interface zone (loose backfill material and excavation disturbed rock) and then the combined backfill-buffer-rock system. Microbial activity and sulfate reduction are low where the buffer or backfill are highly compacted², and therefore it is only considered to occur in the less densely compacted interface zone. The deposition tunnel is represented by a 10 m long section in 2D radial geometry. The geochemistry of the backfill and the buffer is described by considering first only gypsum dissolution and complexation reactions and subsequently adding cation exchange/surface complexation reactions and calcite dissolution/precipitation in a thermodynamic model^{3,4}. The adjacent crystalline rock is represented as an inert homogeneous low-permeability medium, but a case with a high permeability fracture transecting the rock matrix is also considered.

Upon gypsum dissolution sulfate diffuses toward the interface zone where it may be reduced by microbes whose energy source is provided by dissolved organic matter from the backfill or the buffer. Reactive iron (iron oxides, siderite) in the buffer/backfill reacts with sulfide to form mackinawite or pyrite.

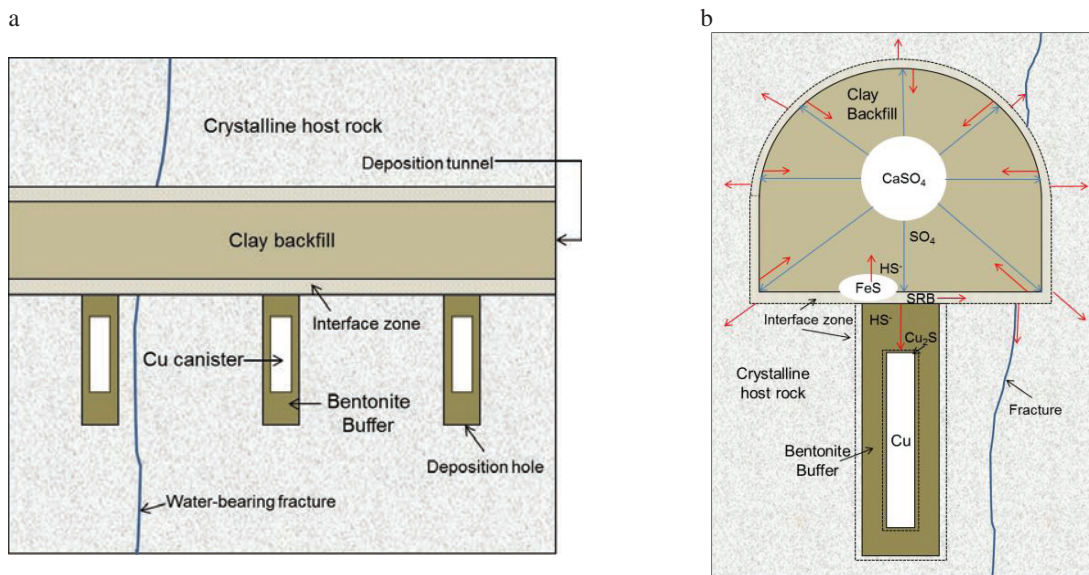


Fig. 1. (a) Layout of the KBS-3 repository in fractured crystalline rock at about 400 m depth; the engineered barrier system (EBS) consists of Cu waste canisters and bentonite buffer emplaced in deposition holes spaced at about 10 m distance in the deposition tunnels (diameter 2.5 m) backfilled with clay materials; (b) cross-section of deposition tunnel and deposition hole sketching sulfate and sulfide fluxes in the EBS.

The model was implemented in the reactive transport code PFLOTRAN⁵. A uniform single diffusion coefficient for all species in the backfill was assumed. In a separate case the effect of multicomponent diffusion and anion exclusion on the results was tested by applying a modified version of FLOTRAN⁶ which explicitly considers diffusion in the electrical double layer (EDL) of the clay. The modelling efforts involved three main parts:

A) *Assessment of gypsum depletion times in the backfill:* First, the effects of different hydraulic conditions in the host rock and the surrounding groundwater without sulfate reduction are considered. Then, the conventional model with a single diffusion coefficient is compared with the multicomponent EDL diffusion model under the premise of instantaneous sulfate reduction in the interface area.

B) *Full implementation of biogeochemical reactions:* The microbial sulfate reduction process is described by simplified Monod kinetics, considering catabolic and anabolic pathways. The reactivity of organic carbon in the clay is largely unconstrained and its effect is therefore assessed by bounding cases. The availability of Fe for reaction with sulfide is controlled by kinetic dissolution of Fe minerals in the clay and Fe(II) diffusion into the interface area. The effect of the dominant buffering Fe-S phase, either mackinawite or pyrite is also explored.

C) Assessment of Cu corrosion rates: The model was then extended to quantify the sulphide fluxes through the bentonite buffer in the deposition hole and to assess the corrosion of the Cu canister. It involved a sequential 2-step approach in which the results from the backfill-rock calculations (part B) were used as input for modelling of the three component backfill-buffer-rock system in 2D radial geometry. The corrosion reaction was implemented as $2\text{Cu} + \text{HS}^- + \text{H}^+ \rightarrow \text{Cu}_2\text{S} + \text{H}_2$, thus every mol of HS^- reaching the canister surface induces the precipitation of 1 mol of Cu_2S (chalcocite) and 1 mol of hydrogen gas.

3. Results and discussion

3.1. Gypsum depletion

The strong sulfate concentration gradient between the backfill porewater and surrounding groundwater induces a diffusive sulfate flux into the rock and a receding gypsum dissolution front in the backfill, ultimately leading to the complete removal of gypsum from the backfill. The most rapid gypsum depletion rate, leading to a minimum gypsum depletion time of about 4000 years, occurs in a high diffusivity rock section – mimicking a high fracture permeability – or by rapid SO_4 reduction in the EDZ (Fig. 2a). The same calculation using the multicomponent EDL diffusion option yields a significantly longer depletion time of 15000 years. This difference is explained by slower diffusion rates of anions and consequently of sulfate due to the anion exclusion effect.

The depletion time strongly depends on the hydraulic conditions in the adjacent rock (Fig. 3b). In rock sections with a reference diffusivity and thus a low fracture permeability around the deposition tunnel, the gypsum depletion rate is predicted to be very slow, that is well above 100,000 years. Owing to focused out-diffusion in the vicinity of a transecting fracture, shorter depletion times are predicted, but these are still on the order of several tens of thousands of years.

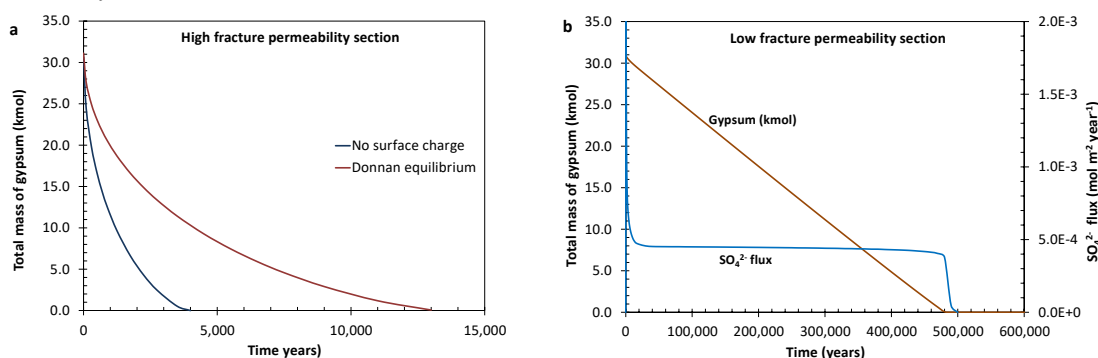


Fig. 2. (a) Evolution of gypsum inventory in backfill for high fracture permeability rock section, comparison between “conventional” single diffusivity model and multicomponent EDL model; (b) Evolution of sulfate fluxes and gypsum inventories for low fracture permeability rock section (single diffusivity model).

3.2. Fate of sulfide and other selected species

Low permeability rock: The rate of biodegradation and hence of sulfide production depends on the reactivity of organic matter in the backfill which in turn controls the DOC in the pore water. The behavior of organic matter is poorly constrained due to the lack of experimental data, but organic carbon in bentonite is expected to be recalcitrant and fairly poorly soluble⁷. Different values for DOC were used to assess the impact on sulfate reduction rates. An increase in DOC increases bacterial activity and the production of sulfide. Concomitantly, the pCO_2 increases and the pH decreases, which favors high sulfide concentrations ($7 \cdot 10^{-5}$ M) in the interface zone. These calculations were based on the assumption of mackinawite being the buffering Fe-S mineral phase. Assuming buffering by the less soluble pyrite, much lower sulfide concentrations are predicted. One consequence of a high dissolution rate of organic C is that the mass of organic C becomes exhausted after about $3 \cdot 10^5$ years. Siderite weathering in the backfill provides an important Fe source which contributes to immobilizing sulfide via Fe-S precipitation. Siderite, however, is predicted to re-precipitate in the interface zone whilst calcite dissolves: $\text{CaCO}_3 + \text{Fe}^{2+} \rightarrow \text{FeCO}_3 + \text{Ca}^{2+}$.

In general, owing to the small amounts of primary accessory minerals, volumetric mineral changes are small indicating overall well buffered conditions.

Effect of high permeability fracture zones: Simulations predict lower sulfide fluxes and smaller geochemical change. This is primarily because of a faster exchange between the clay porewater and the fracture groundwater leading to more moderate changes in pH/pCO₂.

3.3. Sulfide fluxes in bentonite buffer and canister corrosion rates

The sulfide fluxes into the deposition hole and in the buffer towards the canister are controlled by the transport properties of the rock and the conditions in the backfill, in particular the DOC, the rate of bacterial metabolism and the supply of Fe (see above). Thus, in higher permeability rock sections, sulfide fluxes are attenuated and geochemical changes are small compared to low permeability sections. The Cu corrosion rates are directly dependent on these different transport conditions (Fig. 3). Higher corrosion rates are predicted in sections where the rock is tight. In general, however, corrosion rates are small, leaving less than 1 vol% of the total Cu inventory corroded after 10⁶ years.

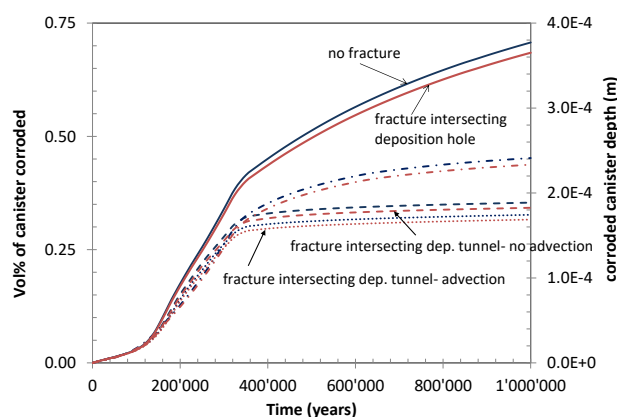


Fig. 3. Volume fraction of canister affected by corrosion (blue curves) and the equivalent corroded canister depth (red curves) for four scenarios. Corrosion rates are deduced from slope of curves.

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